



On the study of KF/Zn(Al)O catalyst for biodiesel production from vegetable oil

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ARTICLE INFO

Article history:

Received 24 November 2009

Received in revised form 15 April 2010

Accepted 7 June 2010

Available online 11 June 2010

Keywords:

Heterogeneous catalyst

Transesterification

Biodiesel

Potassium fluoride

Zn–Al mixed oxides

ABSTRACT

A KF/Zn(Al)O catalyst was prepared by doping KF on calcined Zn–Al hydrotalcite-like compounds and tested for transesterification of vegetable oil with methanol to biodiesel. The obtained catalyst was characterized using techniques of nitrogen physisorption, Hammett indicator, X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). Its catalytic activity was compared with that of Zn–Al hydrotalcite-like compounds, Zn(Al)O, KF, KF/ γ -Al₂O₃ and KF/ZnO. It was found that the prepared KF/Zn(Al)O catalyst showed the highest activity. This catalyst was particularly effective since, for a methanol to oil molar ratio of 6:1, an addition of 3 wt.% KF/Zn(Al)O catalysts, at 65 °C reaction temperatures, the biodiesel yield exceeded 95% at a reaction time of 3 h. Its high activity was ascribed to the formation of new phases KF and KOH and effect of Zn(Al)O support.

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1. Introduction

Biodiesel is a renewable alternative to petroleum diesel that is composed of monoalkyl esters of fatty acids, and it has similar physical properties to petrodiesel but unique advantages including being renewable, biodegradable, non-toxic and low emissions. The production of biodiesel from vegetable oil represents a well-established means of producing liquid fuels from biomass, and one which is rapidly growing in importance [1]. Biodiesel is generally produced by transesterification of vegetable oils or animal fats with short-chain alcohols (generally methanol) in the presence of catalysts [2–5]. The conventional catalysts for this transesterification reaction are homogeneous strong bases (such as alkali metal hydroxides and alkoxides) and homogeneous acids (such as H₂SO₄). However, homogeneous alkaline catalysts are generally corrosive to equipment and also react with free fatty acid to form unwanted soap by-products that require expensive separation; homogeneous acid catalysts are difficult to recycle and operate at high temperatures, and also give rise to serious environmental and corrosion problems. Therefore, the development of solid catalysts has recently gained much attention in view of their ease of separation and lack of corrosion or toxicity problems [6–10].

The use of heterogeneous catalysts that rely on the treatment of various catalyst supports, i.e., porous powders of zeolites, zinc

oxide, alumina with Na, NaOH, KOH, K₂CO₃, KNO₃, KI, KF [11–16], offers various advantages including the recovery and recycling of the catalyst. One of the important methods to prepare heterogeneous catalysts is that of doping KF on one support. The KF doped on Al₂O₃ supports are a kind of solid base catalysts, which have been employed in a variety of organic reaction types with high yields. With many merits involving, e.g., easier preparation, cheapness, easier storage, mild catalytic conditions, easier post work, and high stereoselectivity, it becomes a new environmental protection catalyst. Boz et al. studied the activity of KF loaded nano- γ -Al₂O₃ catalyst for the transesterification of vegetable oil to biodiesel [14]. A methyl ester yield of $97.7 \pm 2.14\%$ was obtained under the catalyst preparation and transesterification conditions of 8 h of reaction time at 338 K, and using 3 wt.% catalysts and molar ratio of methanol/oil of 15:1. KF loaded on ZnO is an active and promising heterogeneous catalyst for the production of biodiesel from soybean oil [13]. When the reaction was carried out at a molar ratio of methanol to soybean oil of 10:1 and a reaction time of 9 h, the yield of biodiesel was 87% over the KF/ZnO catalyst. The reported results showed that the structure and composition of supports affected the activity of the KF supported catalyst in transesterification of vegetable oil to biodiesel.

The structure of Zn–Al mixed oxide may be different with that of pure ZnO and pure Al₂O₃, so the KF on Zn–Al mixed oxide may be a promising catalyst for the transesterification of vegetable oil to biodiesel. Furthermore, the mixed oxide of Zn and Al as a heterogeneous catalyst has been used for the biodiesel production in the industrial scale. The Esterflip-H process developed by the French Institute of Petroleum (IFP) is the only heterogeneous biodiesel process in practice in two 160,000 t/year plants in France and Sweden.

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The process involving a heterogeneous solid catalyst consisted of a mixed oxide of Zn and Al. The reaction is performed at higher temperature and pressure than homogeneous catalysis processes, with an excess of methanol [17–19]. The KF loading on Zn–Al mixed oxide may increase the activity of catalyst evidently. However, to my knowledge, there are no reports about the study of KF on mixed oxide of Zn and Al catalyst.

In the present study, a Zn–Al mixed oxide support was prepared by calcining the Zn–Al hydrotalcite-like compounds precursor. The obtained Zn–Al mixed oxide support was treated with KF to prepare a KF on Zn–Al mixed oxide catalyst. The catalytic properties of the KF on Zn–Al mixed oxide catalyst were tested for the transesterification reaction of vegetable oil with methanol to produce biodiesel.

2. Experimental

2.1. Preparation of catalysts

2.1.1. Preparation of support

Zn–Al hydrotalcite-like compounds with $\text{Al}^{3+}:\text{Zn}^{2+}$ atomic ratios of 1:3 were prepared using a standard aqueous co-precipitation method at constant pH and temperature [20]. An aqueous solution (166 mL) of the metal nitrates in a desired $\text{Al}^{3+}:\text{Zn}^{2+}$ molar ratio with a total concentration of 1.5 M was mixed slowly with continuous stirring with an alkaline solution of $\text{NaCO}_3/\text{NaOH}$. The molar amount of NaCO_3 was twice that of Al^{3+} . The pH value of the mixture was kept constant, typically at values between 9 and 10, by adjusting the flow rate of the alkaline solution. The temperature was maintained at 60 °C. Following this addition, which resulted in the formation of heavy slurry, the mixture was aged at 60 °C for 18 h with stirring, to facilitate the selective growth of the precipitated hydrotalcite phase. The slurry was then cooled to 25 °C, filtered, and washed with water until the pH value of the filtrate was near 7. The precipitate was dried at 90 °C for 16 h. The resulting material was Zn–Al hydrotalcite (hereafter indicated Zn–Al HTLcs). The obtained Zn–Al HTLcs was calcined at 500 °C for 3 h in static air, and then it converted into mixed Zn–Al oxides (hereafter indicated as Zn(Al)O).

To compare the activities of the prepared catalyst with its corresponding pure oxide, ZnO was also prepared by precipitation using aqueous NaOH from its corresponding aqueous nitrate salt solutions followed by calcination in air at 500 °C for 5 h. $\gamma\text{-Al}_2\text{O}_3$ used was a commercial sample (Alfa Aesar).

2.1.2. Preparation of KF supported catalyst

A 80 wt.% (KF to Zn(Al)O weight ratio) KF on Zn(Al)O support was prepared by an impregnation method with an aqueous solution of KF compound synthesized according to the literature procedures [13,21]. The KF on Zn(Al)O catalyst was prepared by the following procedure: a solid Zn(Al)O support (3 g) was mixed with KF (2.4 g) in 15 mL of water, and the resulting solid was dried in an oven at 90 °C for 12 h. The solid was then crushed and calcined in air at 500 °C for 3 h. Similarly 35, 55, 65 and 100 wt.% KF on Zn(Al)O were prepared. The prepared material was termed as KF/Zn(Al)O. A 80 wt.% KF on ZnO and a 80 wt.% KF on $\gamma\text{-Al}_2\text{O}_3$ were also prepared in a similar way. They were termed as KF/ZnO and KF/ $\gamma\text{-Al}_2\text{O}_3$, respectively.

2.2. Precursors and catalysts characterizations

X-ray diffraction patterns were recorded on a D/Max-3C X-ray powder diffractometer (Rigaku Co., Japan), using a Cu–K source fitted with an Inel CPS 120 hemispherical detector.

Infrared transmission spectra were recorded in a range of 400–4000 cm^{-1} by FTIR spectrometer (Bruker Tensor 27, Germany). KBr pellet technique was applied for determining IR spectra of the samples.

The nitrogen adsorption and desorption isotherms were measured at –196 °C using a Micromeritics ASAP 2020 system. Specific surface areas of the catalysts were determined by nitrogen adsorption data in the relative pressure range from 0.06 to 0.30 using the BET (Brunauer–Emmett–Teller) equation. Total pore volumes were estimated from the amount of nitrogen adsorbed at a relative pressure of 0.992. Pore volume and pore size distribution curves were obtained from the analysis of the desorption branches of the nitrogen isotherms using the BJH (Barrett–Joyner–Halenda) method.

Hammett indicator experiments were conducted to determine the basic strength of each catalyst. The Hammett indicators used were methyl yellow ($\text{pK}_a = 3.3$), neutral red ($\text{pK}_a = 6.8$), bromothymol blue ($\text{pK}_a = 7.2$), phenolphthalein ($\text{pK}_a = 9.3$), alizarin yellow R ($\text{pK}_a = 11.0$), indigo carmine ($\text{pK}_a = 12.2$), 2,4-dinitroaniline ($\text{pK}_a = 15$), 4-nitroaniline ($\text{pK}_a = 18.4$), 4-chloroaniline ($\text{pK}_a = 26.5$), and diphenylmethane ($\text{pK}_a = 35$). Typically, 25 mg of the catalyst was mixed with 5 mL of a solution of Hammett indicators diluted with cyclohexane and allowed to sit for at least 1 h. After the equilibration, the color of the catalyst was noted. The basic strength of the catalyst was taken to be higher than the weakest indicator that underwent a color change and lower than the strongest indicator that underwent no color change. To measure the basicity of solid bases, the method of Hammett indicator–benzene carboxylic acid (0.02 mol/L anhydrous ethanol solution) titration was used.

2.3. Reaction procedure

The reactions were carried out in a batch reactor under vigorous stirring. Typical reactions were performed with 19.6 mL of vegetable oil (100% soybean oil; Xi'an Jiali Grease Industrial Co. Ltd., Xi'an, China) and 4.6 mL of methanol (methanol to vegetable oil molar ratio 6:1) using 3 wt.% (catalyst to oil weight ratio) of KF/Zn(Al)O catalyst at methanol reflux temperature for the specified time. The reaction products were analyzed using the following procedure. The samples were separated from catalyst and glycerol by centrifuge. The glycerol could be separated because it was insoluble in the esters and had a much higher density. Then methanol was removed using a vacuum pump and the obtained product were added to deuterated chloroform for ^1H NMR to determine the yield to methyl ester.

3. Results and discussion

3.1. XRD analysis

Fig. 1 displays the XRD patterns of Zn–Al HTLcs, Zn(Al)O and KF/Zn(Al)O. The Zn–Al HTLcs sample showed the typical X-ray diffractograms of HTLcs, with characteristic diffraction peaks at 11.4°, 23.0°, 34.9° (Fig. 1a) [22]. The thermal pre-treatment resulted in a change in the XRD pattern, caused by the removal of CO_2 and H_2O from the starting material. The Zn(Al)O displayed diffraction reflections characteristic of ZnO. No characteristic diffraction peak of Al_2O_3 was observed, suggesting that Al_2O_3 was well mixed with ZnO (Fig. 1b). The XRD patterns of KF/Zn(Al)O showed, in addition to Zn(Al)O, a series of new diffraction peaks (Fig. 1c). Among them, the peaks at 33.5° may be corresponding to the new crystal phase (KF), which was residual phase of KF remained on the composite. The peaks at 29.8°, 42.9° and 53.1° would belong to the new crystal phase (K_3AlF_6). The new crystal phase (K_3AlF_6) may be ascribed to the chemical reaction between KF and the Zn(Al)O support (Eq. (1)) in the process of preparing KF/Zn(Al)O catalysts.



The reaction also showed that KOH was produced when KF was loaded on the Zn(Al)O support. However, no XRD diffraction

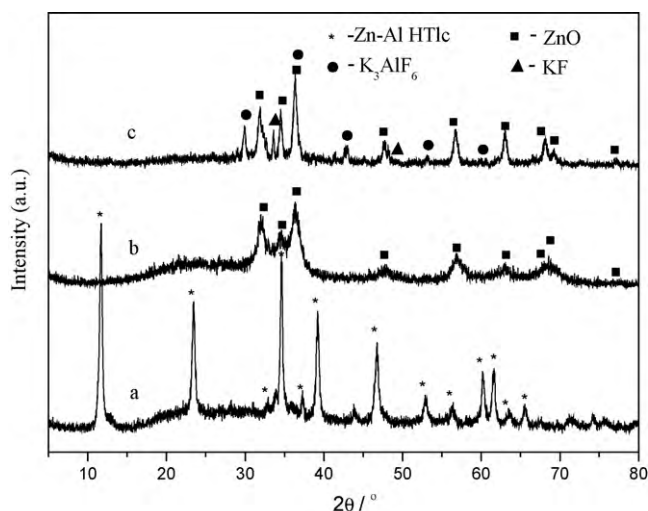


Fig. 1. XRD patterns of (a) Zn-Al HTlcs, (b) Zn(Al)O and (c) KF/Zn(Al)O catalysts.

reflections characteristic of KOH was found in the XRD pattern of KF/Zn(Al)O catalysts. It suggested that the produced KOH was well dispersed on the Zn(Al)O support.

Fig. 2 exhibits the XRD patterns of the prepared ZnO and KF/ZnO catalysts. The ZnO sample showed the typical X-ray diffractograms of ZnO (Fig. 2a). The XRD pattern of KF/ZnO showed, in addition to ZnO, diffraction peaks ascribed to KF, suggesting a residual phase of KF remained on the composite (Fig. 2b). The results also suggested that no other new crystals were produced in the process of preparing KF/ZnO catalysts.

Fig. 3 shows the XRD patterns of the γ -Al₂O₃ and KF/ γ -Al₂O₃. The γ -Al₂O₃ sample showed the typical X-ray diffractograms of γ -Al₂O₃ (Fig. 3a). The XRD pattern of KF/ γ -Al₂O₃ showed, in addition to γ -Al₂O₃, diffraction peaks ascribed to new crystal phase K₃AlF₆ (Fig. 3b). The new crystal phase K₃AlF₆ was produced from a reaction between KF and the γ -Al₂O₃ support (Eq. (1)) happened in the process of preparing KF/ γ -Al₂O₃ catalysts.

Compared the XRD patterns of KF/Zn(Al)O (Fig. 1c), KF/ZnO (Fig. 2b) and KF/Al₂O₃ (Fig. 3b), it can be found that the structure of KF/Zn(Al)O bore, in addition to the crystalline, the features of both KF/ZnO and KF/ γ -Al₂O₃. The KF/Zn(Al)O possessed the new crystal phases K₃AlF₆ and KF. The K₃AlF₆ could be found in KF/ γ -Al₂O₃, and KF in KF/ZnO. The support of KF/Zn(Al)O possessed the structure of

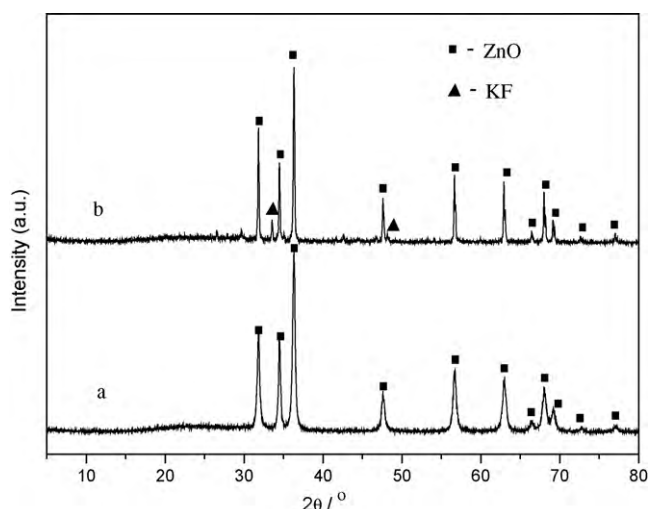


Fig. 2. XRD patterns of (a) ZnO and (b) KF/ZnO catalysts.

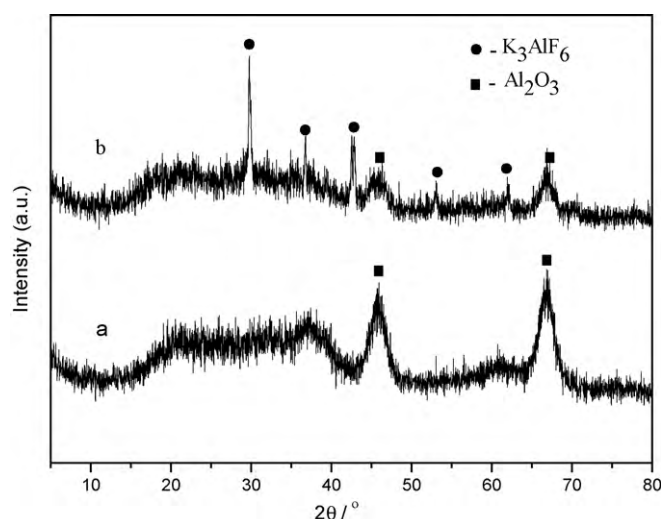


Fig. 3. XRD patterns of (a) γ -Al₂O₃ and (b) KF/ γ -Al₂O₃ catalysts.

crystalline ZnO and amorphous Al₂O₃, which were less crystalline than the supports of KF/ZnO and KF/ γ -Al₂O₃.

3.2. FTIR analysis

Fig. 4a showed the IR spectra of Zn-Al HTlcs, Zn(Al)O and KF/Zn(Al)O. The IR spectra of the sample Zn-Al HTlcs indicated that they were all typical pure hydrotalcites. Two bands at 1630 and 3440 cm⁻¹ were attributed to the OH vibration, assigning to OH in the layer and physically absorbed water. The bands at 774, 1365 and 1499 cm⁻¹ were due to the vibration of CO₃²⁻, indicating the existence of CO₃²⁻ between the layers. The bands around 400–600 cm⁻¹ were due to Zn–O–H and Zn–Al–O–H vibration [23–25]. The infrared spectrum of Zn(Al)O showed bands assigned to Zn(Al)O (bands around 474 and 780 cm⁻¹), and bands to physically absorbed water (bands at 1620 and 3440 cm⁻¹). For KF/Zn(Al)O, the infrared spectrum showed, in addition to features to Zn(Al)O and water, bands assigned to K₃AlF₆ (bands at 577 cm⁻¹), and bands to potassium carbonate (bands at 841, 1002, 1410, 1490 and 1574 cm⁻¹). The bands assigned to K₃AlF₆ proved the presence of K₃AlF₆ on the surface of KF/Zn(Al)O catalyst, which supplied the further evidence for Eq. (1). The potassium carbonate may be produced from the reaction between CO₂ adsorbed from the air and KOH from Eq. (1).

The investigation of the Zn(OH)₂, the support ZnO and KF/ZnO catalysts was conducted via IR spectroscopy as shown in Fig. 4b. For Zn(OH)₂, the support ZnO and KF/ZnO catalysts, there are two absorption bands at 3440 and 1640 cm⁻¹ assigned to the physically absorbed water. For the KF/ZnO catalysts, the intensity of the bands at 3440 and 1640 cm⁻¹ became stronger than the support ZnO, which indicated that KF could simply introduce hydroxyls at the surface of ZnO [13].

The infrared spectrum of γ -Al₂O₃ showed features due to γ -Al₂O₃ and water (Fig. 4c). For KF/Al₂O₃, the infrared spectrum showed, in addition to features to γ -Al₂O₃ and water, bands readily assigned to potassium carbonate (bands at 771, 860, 1010, 1413, 1540 cm⁻¹), and bands to hexafluoroaluminate (bands at 577 cm⁻¹) [26].

3.3. BET surface area and pore size

Fig. 5 shows nitrogen physisorption isotherms and BJH pore size distribution for Zn(Al)O, ZnO and γ -Al₂O₃. The isotherm of ZnO has the characteristic type III shape (Fig. 5b). The BJH pore diam-

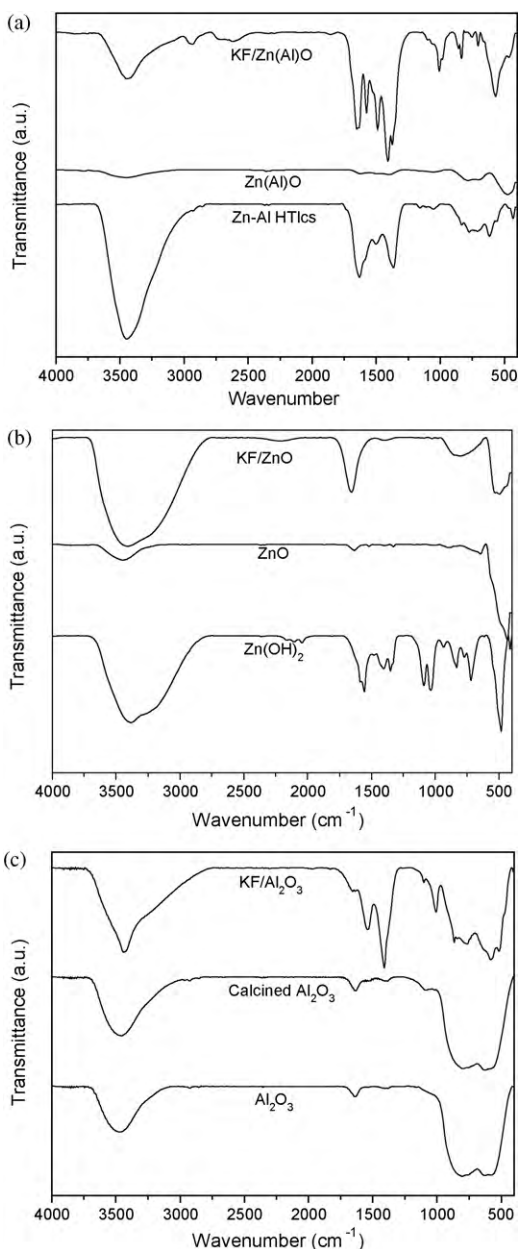


Fig. 4. FTIR spectra of samples (a) Zn–Al HTlcs, Zn(Al)O, KF/Zn(Al)O; (b) Zn(OH)₂, ZnO, KF/ZnO; (c) γ -Al₂O₃ as received, calcined γ -Al₂O₃, KF/ γ -Al₂O₃.

eters and the specific BET surface areas as well as pore volumes confirmed that ZnO was an impermeable material. The isotherm of γ -Al₂O₃ has the characteristic type IV shape (Fig. 5c and Table 1). The type IV isotherm and pore size distribution suggested that γ -Al₂O₃ was one mesoporous material. Zn(Al)O catalyst also shows the characteristic type IV isotherm (Fig. 5a). Compared with that of γ -Al₂O₃, the pore size distribution of Zn(Al)O was more concen-

Table 1
Nitrogen physisorption data of the three catalyst supports.

Sample	Surface area ^a (m ² g ⁻¹)	Pore diameter ^b (nm)	Pore volume ^b (cm ³ g ⁻¹)
Zn(Al)O	102	18.8	0.32
ZnO	7	32.1	0.08
γ -Al ₂ O ₃	272	8.0	0.79

^a Calculated by the BET method.

^b Calculated by the BJH method from the desorption isotherm.

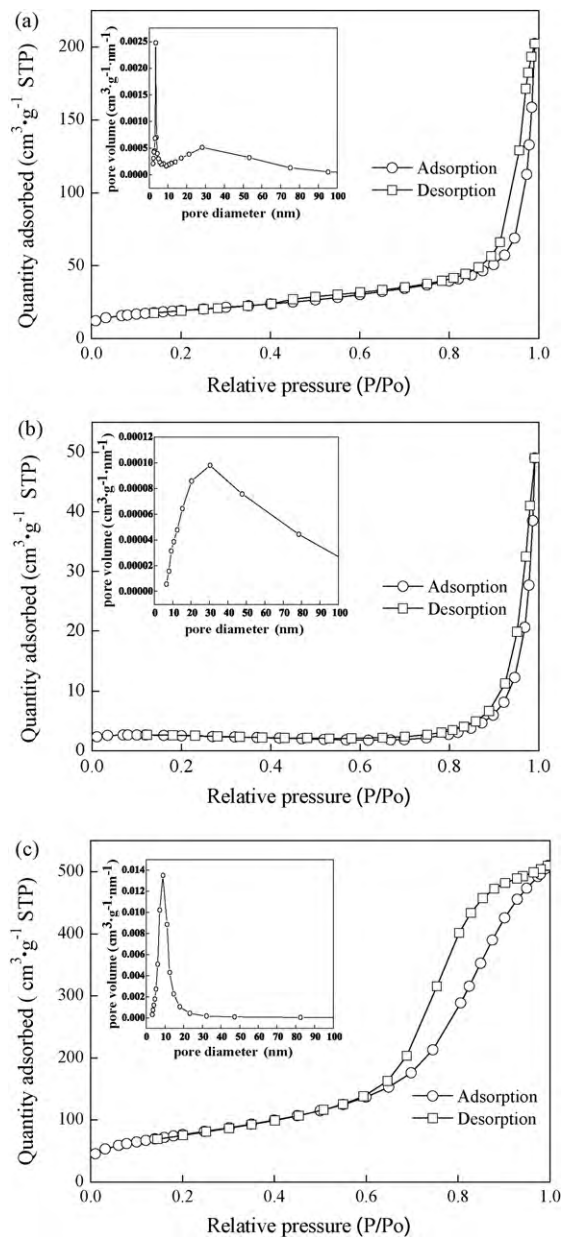


Fig. 5. Nitrogen physisorption isotherms (○, adsorption; □, desorption) and BJH pore size distribution for (a) Zn(Al)O, (b) ZnO, and (c) γ -Al₂O₃.

trated and pore diameter was smaller. The surface area of the three catalyst supports decreased in the order γ -Al₂O₃ > Zn(Al)O > ZnO (Table 1).

3.4. The basic strengths and basicity of the catalysts

The strength of the basic sites in the solids was analyzed qualitatively using Hammett indicators. As shown in Table 2, the Zn–Al HTlcs, Zn(Al)O, ZnO and γ -Al₂O₃ samples were found to be weak basic, possessing H_v values in the range 9.3–11. Loading KF onto the support material promoted basic strengths of the catalysts. The KF/Zn(Al)O possessed H_v values in the range 15–18.4, while KF/ZnO was less basic with H_v values in the range 12.2–15, KF/ γ -Al₂O₃ was more basic, as evidenced by their ability to effect a color change with 4-nitroaniline (pK_a = 18.4). The basicity of solid bases was also measured. The total basicity of the KF doped catalyst was higher than that of the unloaded support. The results suggested that load-

Table 2
Results of Hammett indicator measurements on catalysts.

Sample	Basic strength	H _a = 7.2–9.3	H _a > 9.3	Total basicity (mmol g ⁻¹)
Zn–Al HTlcs	9.3 < H _a < 11	0.09	0.26	0.35
Zn(Al)O	9.3 < H _a < 11	0.27	0.41	0.68
ZnO	9.3 < H _a < 11	0.11	0.05	0.16
γ-Al ₂ O ₃	9.3 < H _a < 11	0.1	0.61	0.71
KF/Zn(Al)O	15 < H _a < 18.4	1.38	0.76	2.14
KF/ZnO	12.2 < H _a < 15	1.12	0.72	1.84
KF/γ-Al ₂ O ₃	18.4 < H _a < 26.5	0.16	2.16	2.32

ing KF onto the support material promoted the basic strengths and basicity of the catalysts.

3.5. Influence of the loading amount of KF on support

Fig. 6 shows the influence of the KF loading ratio of KF/Zn(Al)O on biodiesel yield. Under the same reaction condition, as the loading amount increased, the biodiesel yields also increased. When loading amount of KF reached 80 wt.%, the maximum biodiesel yield was obtained. Therefore, 80 wt.% was selected as the optimum loading ratio of KF/Zn(Al)O catalyst for transesterification of vegetable oil with methanol to biodiesel.

3.6. Transesterification over KF/Zn(Al)O catalysts

3.6.1. Effect of reaction variables

The catalytic activity of KF/Zn(Al)O catalysts was tested for the transesterification reaction of vegetable oil with methanol into biodiesel. The yield of biodiesel was affected by reaction variables, such as methanol/oil ratio, catalyst amount or reaction time. The reaction variables were associated with the type of catalysts used [3]. Therefore, the effect of reaction variables was studied in the presence of KF/Zn(Al)O catalysts. For the following transesterification of vegetable oil with methanol to biodiesel, the reaction temperature was set at 65 °C, which was normally used in the homogeneous catalytic system.

The experimental results showed that the yield increased with increasing the methanol/oil molar ratio, and reached >95% when the ratio was above 6 (Fig. 7). As shown in Fig. 8, the yield increased with increasing the catalyst loading weight. The yield was more than 95% when the catalyst loading weight is above 3 wt.%. Fig. 9

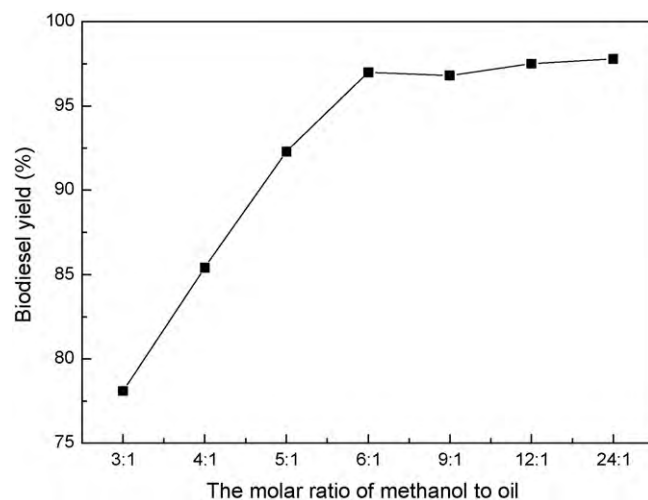


Fig. 7. Effect of the molar ratio of methanol to oil on the biodiesel yields. Reaction conditions: catalyst amount, 3 wt.%; reaction temperature, 65 °C; reaction time, 3 h.

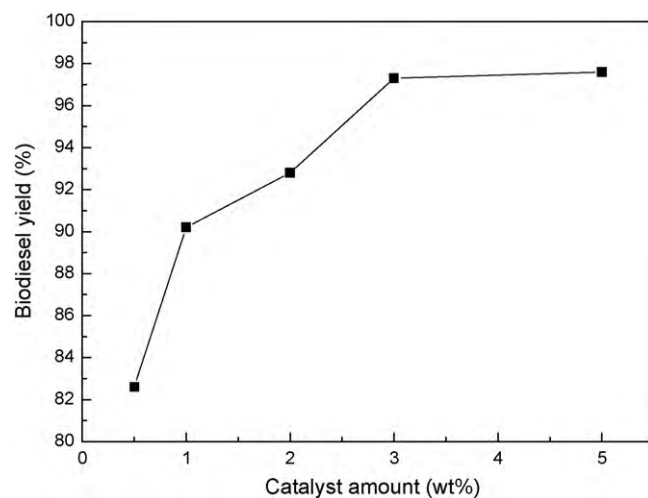


Fig. 8. Effect of catalyst amount on biodiesel yields. Reaction conditions: methanol to oil molar ratio, 6:1; reaction temperature, 65 °C; reaction time, 3 h.

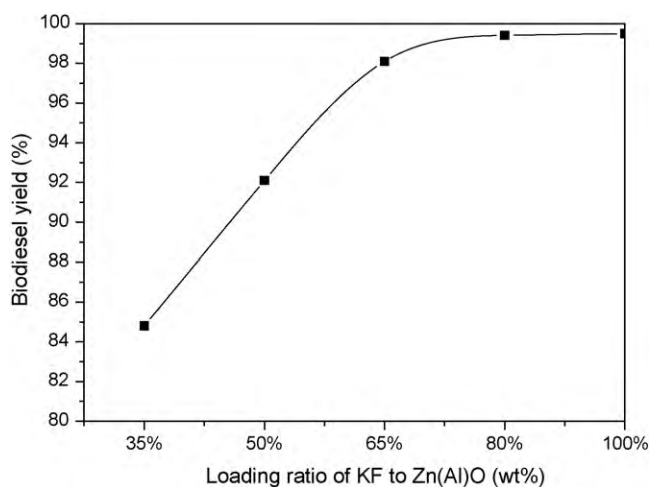


Fig. 6. Effect of the loading ratio of KF/Zn(Al)O on the biodiesel yields. Reaction conditions: catalyst amount, 3 wt.%; methanol to oil molar ratio, 6:1; reaction temperature, 65 °C; reaction time, 3 h.

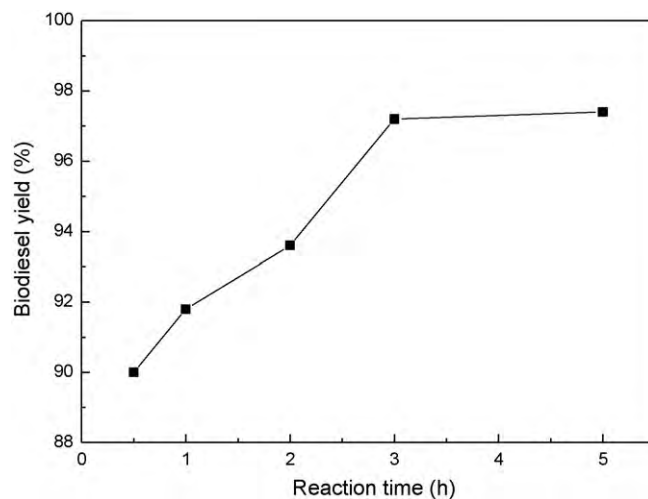


Fig. 9. Effect of reaction time on biodiesel yields. Reaction conditions: catalyst amount, 3 wt.%; methanol to oil molar ratio, 6:1; reaction temperature, 65 °C.

Table 3
Biodiesel yields over different catalysts.

Catalysts	Biodiesel yield (%)
Zn–Al HTlcs	3
Zn(Al)O	8
ZnO	<1
γ -Al ₂ O ₃	<1
KF	<1
KF/Zn(Al)O	95
KF/ γ -Al ₂ O ₃	80
KF/ZnO	60

shows the yield change versus time. The yield increased with time, reaching maximum value (yield >95%) after 3 h.

3.6.2. A comparative study

The catalytic activity of KF/Zn(Al)O catalysts was compared with that of Zn–Al HTlcs, Zn(Al)O, KF (Table 3). The reactions were carried out in the condition as following: methanol to oil molar ratio of 6:1, mass of catalyst of 3%, reaction time of 3 h, and reaction temperature of 65 °C. It was found that Zn–Al HTlcs, Zn(Al)O and KF showed low activity, with yield <8%. The biodiesel yield (>95%) was much higher when catalyzed by KF/Zn(Al)O catalyst, which suggested that the load of KF on Zn(Al)O support largely increased the activity of the catalyst.

The catalytic property of prepared KF/Zn(Al)O catalyst was also compared with that of KF/ γ -Al₂O₃ and KF/ZnO (Table 3). Under the same reaction conditions, above 95% biodiesel yield was obtained in the presence of KF/Zn(Al)O catalyst, 85% biodiesel yield in KF/ γ -Al₂O₃ catalyst and 60% biodiesel yield in KF/ZnO catalyst. Therefore, the catalytic activity of the three KF doped catalysts decreased as follows: KF/Zn(Al)O > KF/ γ -Al₂O₃ > KF/ZnO. Since the three catalysts were prepared by the same method, the difference of their activity may be ascribed to effect of the catalyst supports. The results showed that the effect of the catalyst supports decreased as follows: Zn(Al)O > γ -Al₂O₃ > ZnO, suggesting that the Zn(Al)O support are more beneficial than pure γ -Al₂O₃ and ZnO support for the preparation of high active KF doped catalysts.

Both the KF/Zn(Al)O and KF/ γ -Al₂O₃ possessed the new crystal phases K₃AlF₆, suggesting that the same chemical reaction (Eq. (1)) happened in the process of preparing these two catalysts. Therefore, for both the KF/Zn(Al)O and KF/ γ -Al₂O₃ catalysts, KOH was formed in the initial preparation of the solid supported material by reaction of KF with the alumina support. The published articles about KF/Al₂O₃ supplied helpful experimental results for clarification of catalytic mechanism of KF/Zn(Al)O catalyst.

The versatile reagent KF/Al₂O₃ was originally introduced in 1979 by Ando et al. as a useful agent for inducing alkylation reactions. It possesses a number of the advantages of both solution and solid phase chemistry. Additional benefits have been achieved by taking advantage of the strongly basic nature of KF/Al₂O₃, which has allowed it to replace organic bases in a number of reactions including but not limited to selective *N*-alkylation of amides, epoxidations, diazotizations, Sonogashira couplings, Suzuki couplings, Knoevenagel reactions, and Horner–Emmons chemistry. In contrast to many applications of KF/Al₂O₃ to organic syntheses as a base catalyst, mechanisms of the appearance of the basicity of KF/Al₂O₃ are not clarified [27,28]. The source of this basicity has been the subject of some debate in the literature. Weinstock et al. have argued that KF/Al₂O₃ derives its basicity from the formation of KOH in the initial preparation of the solid supported material by reaction of KF with the alumina support (Eq. (1)) [26]. However, Ando et al. have disputed this claim. They examined a number of samples of KF/Al₂O₃ by titrimetric analysis. Aqueous washing of the samples provided an alkaline solution which could be titrated to

Table 4
Recycling experiments for KF/Zn(Al)O catalyst.

Entry	Catalyst	Biodiesel yield (%)
1	KF/Zn(Al)O (1st use)	97
2	KF/Zn(Al)O ^a (2nd use)	61
3	KF/Zn(Al)O ^a (3rd use)	7
4	KF/Zn(Al)O ^a (4th use)	<1
5	KF/Zn(Al)O ^b (5th use)	98

^a The used KF/Zn(Al)O catalyst was separated from the reaction solution by centrifugation. It was taken as the catalyst for the repeated reactions. The repeated reactions were run under the same reaction conditions to the last reaction.

^b After fourth use, the KF/Zn(Al)O catalyst was reloaded with KF. The loading method was same to that of preparing fresh KF/Zn(Al)O catalyst. The reloaded catalyst was used as catalyst for the fifth repeated reaction.

determine the amount of soluble base present. They also separately washed samples with a fixed excess of aqueous HCl, to determine the overall basicity of the samples. The total basicity was found to be significantly higher than could be accounted for by the formation of KOH during reagent preparation. Ando et al. concluded that there are three basic species or mechanisms of the appearance of the basicity of KF/Al₂O₃ [29]: (1) the presence of active fluoride, (2) the presence of [Al–O[–]] ion which generates OH[–] when water is added, and (3) the cooperation of F[–] and [Al–OH]. This opinion was widely accepted by peers and supported by experiments results from peers. Hattori et al. reported that the KF/Al₂O₃ surface species of relevant to the catalytic activities, in particular for the double bond isomerization and Tishchenko reaction, is the F[–] containing species which gives a peak at –150 ppm in ¹⁹F MAS NMR [30]. More recently, Parvulescu et al. investigated the evidences of the nature of the active site and catalytic performances on basic large mesoporous alumina supported alkaline fluorides for transesterification of vegetable oils [27]. Their results stated that the active site of alumina supported alkaline fluorides is thought to be the consequence of the cooperation between the fluorine and oxygen.

In this paper, KF showed an interesting promoting effect, added to Zn(Al)O, in the transesterification of soybean oil to biodiesel. The promoting effect of KF was operative also by using ZnO and Al₂O₃ as supports. As a matter of fact, K₃AlF₆, KF and KOH were formed during the treatment of Al₂O₃ and Zn(Al)O with KF. K₃AlF₆ is mainly formed with pure Al₂O₃ and Zn(Al)O. Moreover, KF with ZnO gave promoting effect without the presence of K₃AlF₆. Therefore, K₃AlF₆ was not the active component of the KF/Zn(Al)O catalyst. Very probably also ZnO gave place to a leaching effect forming a soluble alkoxide, giving a contribution of homogeneous catalysis. ZnO and Zn(Al)O showed low activity, with yield <8% (Table 3). This result suggested that the eventual effect of ZnO leaching and related consequences could be neglected. Referenced to the mechanisms of KF/Al₂O₃ catalyst, the active sites of the KF/Zn(Al)O catalyst may be (1) the presence of active fluoride, (2) the presence of [Al–O[–]] ion which generates OH[–] when water is added, and (3) the cooperation of F[–] and [Zn(Al)–OH].

3.6.3. Recycling experiments for KF/Zn(Al)O catalyst

Recovery and reuse of the catalyst is an important factor in the economics of the use of the heterogeneous catalysis process for biodiesel manufacture. We attempted to reuse the catalyst by two methods (Table 4). Direct reuse of the catalyst (Table 4, entry 2) led to a greater than 30% decrease in activity. The catalyst was completely deactivated after being used more than 4 times. The reusability of KF/Zn(Al)O catalyst was similar to other KF doped catalyst [14]. In our future work, further study will be conducted to investigate how to increase the reusability of KF/Zn(Al)O catalyst. However, we found that by reloading KF on the used catalyst, the catalyst could be recovered and reactivated (Table 4, entry 5). The

results suggested that the activity of KF/Zn(Al)O catalyst could be regenerated in a simple method.

4. Conclusions

High active KF/Zn(Al)O catalyst was firstly prepared by loading KF on calcined Zn–Al HTlcs supports. It was proved that the activity of KF/Zn(Al)O catalyst was higher than that of KF/ γ -Al₂O₃ and KF/ZnO. In addition to biodiesel production, the prepared active KF/Zn(Al)O catalyst should find application in a wide range of other base-catalysed important organic reactions.

Acknowledgement

This work was supported by the Scientific Research Foundation for the Returned Overseas Chinese Scholars and the Fundamental Research Funds for the Central Universities, State Education Ministry.

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